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NON-RADIATIVE TRANSITIONS DURING THE DECAY OF A PHOSPHOR

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ABSTRACT. The decay of zinc sulphide phosphors at different temperatures using ultraviolet excitation has been measured. It is found that the decay constant decreases with temperature. This is theoretically explained by using the idea of non-radiative transitions during the decay. Efficiency of phosporescence during decay is also discussed.

INTRODUCTION

Randall and Wilkins (1945) and Garlick and Gibson (1948) developed a theory to explain the various phenomena of phosphorescence by assuming the storage of excited electrons in metastable energy levels due to traps arising from the co-activator atoms or lattice defects of the crystal. The existence of these electron traps is responsible for the slow rise of fluorescence, of phosphorescence of glow emission, of infra-red stimulation and quenching. In spite of extensive studies in the field of solid-state luminescence by various workers, it has not yet been possible to explain the luminescence phenomena satisfactorily. The present experiments were conducted to study the decay properties at different temperatures and also the efficiency of phosphorescence.

EXPERIMENTAL

(A) *Preparation of zinc sulphide phosphor*

Zinc sulphide of high purity was prepared. Triply distilled water and pyrex containers were used throughout. Small quantities of copper in the form of copper sulphate (Analar B.D.H.) were added to the zinc sulphide and then dried at 110°C in an oven. The dried material was put in a clean fireclay boat and placed in the hottest zone of a tubular silica furnace. A constant stream of pure dry H_2S was allowed to flow through this furnace and the temperature maintained at 1100°C for half-an-hour. Under these conditions the phosphors produced were of reasonably reproducible quality.

(B) *Apparatus*

The phosphor was excited by a mercury discharge bulb operated by a stabilized voltage supply. By the use of proper filters the 3600 Å line was allowed to fall

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on the phosphor. To measure the intensity of phosphorescence and its decay, a RCA 931 A photomultiplier was used in conjunction with a Hilger galvanometer. A wratten 2A filter was placed in front of the photo-multiplier to exclude the direct light from the mercury bulb. For work at room temperature and above the phosphor was painted on a $1''\times1''$ copper plate with sodium silicate as binder. The plate was held at an angle of 45° to the incident beam. The temperature of the phosphor was measured by a copper-constantan thermo-couple and potentiometer arrangement.

Experiment I : Decay at different temperatures.

RESULTS AND DISCUSSIONS

The variation of the intensity of phosphorescence, I with time t was observed at different temperatures. The intensity was measured in terms of the galvanometer deflection θ and plotted against $1/t$ which gave a straight line (Fig. I.)

$$\text{i.e. } \times I\alpha\theta = \frac{B}{t}$$

Where B is the decay constant and is given by the slope of the straight line. The various values of the slope at different temperatures are given in Table I.

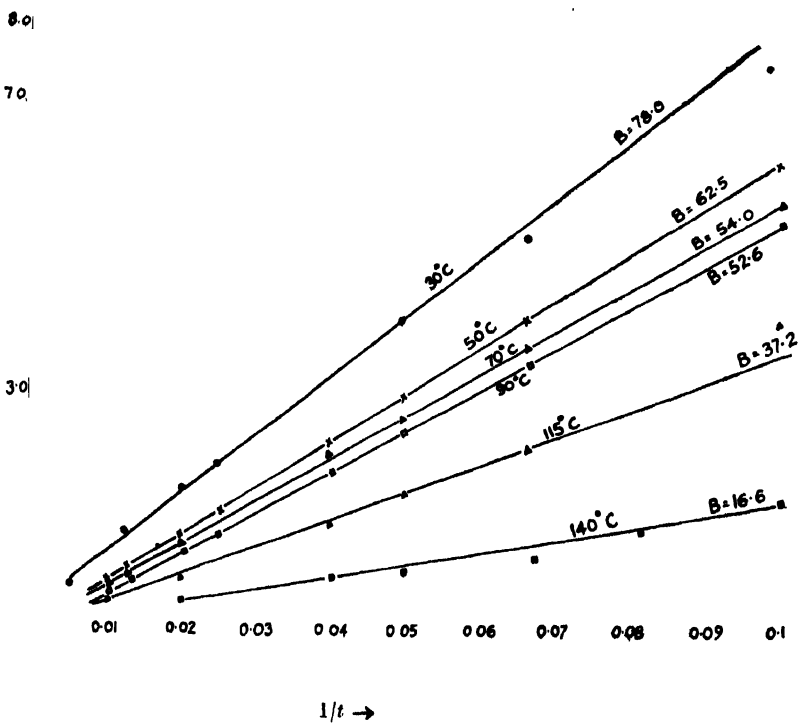

Fig. 1. Decay of ZnS phosphor at different temperatures.

From Table I we find that as the temperature increases the slope B decreases. This cannot be explained by the existing equation (3),(4) of decay,

$$I = \frac{N_E kT}{t}$$

Where T is the temperature in absolute units

k is Boltzman constant

N_E is the number of electrons in each trap.

TABLE I

Calculated values of slope at different temperatures

S/No.	Name of phosphor	Temperature	Value of slope
1		30°C	78.0
2		50°C	62.5
3	ZnS	70°C	54.0
4	'a'	90°C	52.6
5		115°C	37.3
6		140°C	16.6

EFFECT OF NON-RADIATIVE TRANSITIONS

Assuming that during the decay non-radiative transitions are also δ taking place, it is explained that the decay constant decreases with temperature as follows. The general equation for the light emission during decay may be written as :

$$0 = L + Q + \frac{dn_t}{dt} + \frac{dn_c}{dt} \qquad \ldots (1)$$

where L = number of electrons/cm^3 recombining per second radiatively.

Q = number of electrons/cm^3 recombining per second non-radiatively.

n_t = number of electrons/cm^3 in traps

n_c = number of electrons/cm^3 in the conduction band

for $n_t >> n_c$

$$0 = L + Q + \frac{dn_t}{dt} \qquad \ldots (2)$$

It can be shown that during decay non-radiative transitions are proportional to radiative transitions at any instant.

i.e. $Q_{(T)} = KL_{(T)}$ where K is a constant.

Thus equation (2) will become

$$0 = L + KL + \frac{dn_t}{dt}$$

or $$\frac{dn_t}{dt} = -L[1+K]$$

Now $$L = nse^{-E/kT}$$

where s = is a escape frequency

k = Boltzman constant

T = Temperature in absolute unit.

$$\therefore \quad \frac{dn}{dt} = -ns(1+k)e^{-E/kT}$$

Integrating and putting $t = 0$, $n = n_0$ we get

$$n = n_0 \exp[-st(1+K)e^{-E/kT}] \quad \ldots (3)$$

Now, the intensity of phosphorescence during decay is,

$$L = nse^{-E/kT} \quad \ldots (4)$$

substituting the value of n from (3) we get

$$L = n_0 s \operatorname{Exp}[-st(1+K)e^{-E/kT}]e^{-E/k}$$

If there are $N_E dE$ traps with energy lying between E and $E+dE$, then the phosphorescence intensity (I_t) at time t, after cessation of excitation, will be

$$I_t = N_E s \int_0^{\infty} \operatorname{Exp}[-st(1+K)e^{-E/kT}]e^{-E/kT}dE \quad \ldots (5)$$

or $$I_t = \frac{N_E kT}{(1+K)t}$$

or $$\theta = \frac{N_E kT}{c(1+K)t} = \frac{B}{t}$$ where c is a constant

or $$B = \frac{N_E kT}{c(1+K)} \quad \ldots (6)$$

The value of constant B does not vary linearly with temperature as K, the ratio of non-radiative and radiative transitions is also affected by temperature. If the different values of B from Table I and their corresponding temperatures are substituted in (6), we get the values of $c(1+K)/kN_E$ at different temperature as listed in Table II.

From Table II, it becomes clear that K can be expected to increase with temperature and thus it is easy to see that B the decay constant might decrease with temperature.

TABLE II

S/No.	T in absolute unit	$C(1+K)/N_E k$
1	303	3.8
2	323	5.1
3	343	6.3
4	363	6.9
5	388	10.4
6	413	24.8

Experiment II : Efficiency of phosphorescence

Zinc sulphide phosphor was first de-excited completely by heating and by infra-red. The phosphor was then excited at room temperature until the maximum intensity was reached. The excitation was then removed and the phosphor was allowed to decay for some time, and then excitation was recommenced. The ratio of the phosphorescent area P to the deficiency area D_P (Fig. 2) obtained

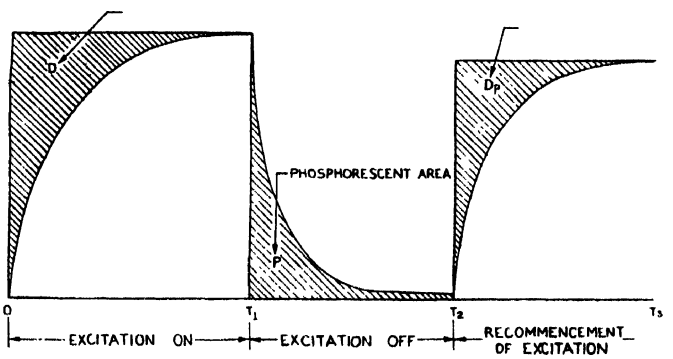

Fig. 2. Experiment of the deficiency area during the rise following the decay (Deflection vs time in second)

TABLE III

Ratio of phosphorescent area of zinc sulphide phosphor to corresponding deficiency area after recommencement of excitation at room temperature

S.No.	Time of decay	P def. sec.	D def. sec.	D_P def. sec.	$\frac{P}{D_P}$
1	15 seconds	40	620	42	.95
2	½ minute	64	620	70	.90
3	1 minute	74	620	99.2	.82
4	3 minutes	94	620	125	.75

during the rise following the decay was determined. Results of this experiment are summerized in Table III, where D is the deficiency area for the completely de-excited sample.

DISCUSSION

The value of P/D_P is nearly one for 15 seconds decayed-phosphor and then decreases with the increase of the decay period. From this result it can be concluded that the efficiency of phosphorescence at room temperature in the begining of the decay is of the same value as that of fluorescence. The decrease of P/D_P with prolonged-decay period may be due to the increase of non-radiative transitions during recommencement of excitation.

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